Pressure effects in the microwave plasma growth of polycrystalline diamond

A. B. Harker and J. F. DeNatale

Rockwell International Science Center
19 Camino Dos Rios, Thousand Oaks, CA 91360

ABSTRACT

Microwave plasma deposition of polycrystalline diamond is being investigated over the pressure range 1 to 100 kPa. The conditions of growth, microstructure, and spectroscopic properties of the resulting materials are being compared. A phenomenological description of the dependence of diamond microstructure upon growth conditions has been developed.

1. INTRODUCTION

Microwave plasma assisted CVD (MPACVD) deposition of polycrystalline diamond has been studied extensively in this and other laboratories in low pressure growth systems at temperatures from 250 to 1100°C with a range of hydrocarbon sources (e.g., CH_4, CO, CH_3OH, C_3H_4O, etc).[1,2,3] These 2.45 GHz systems typically produce a fairly diffuse plasma at pressures of 1 to 5 kPa, providing CVD type growth. At higher plasma pressures, the three body recombination of electrons with ions becomes dominant, greatly limiting the geometric area of the plasma. Visually, the plasma shrinks to the center of the chamber with increasing pressure and eventually cannot be sustained.

To produce a microwave plasma at higher pressures, other cavity designs which produce sufficient energy density to achieve and sustain gas breakdown must be used. We have investigated the use of a custom designed TM_{010} cylindrical 2.45 GHz cavity to develop sustained plasmas and diamond growth at pressures in excess of one atmosphere. At higher pressures, diamond particles nucleate with line of sight relationship to the plasma source with a higher temperature dependence for diamond growth than observed under lower pressure CVD conditions. The microstructures of the diamond films produced in the low and high pressure systems can be related in the same manner to the growth controlling parameters.

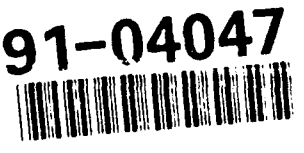
2. EXPERIMENTAL

Diamond films were grown in two different flow systems both using an Applied Science 1.5kW, 2.45GHz magnetron source and waveguide arrangements. All substrate surfaces were prepared by diamond paste abrasion before deposition.

The low pressure cavity is an all-metal sealed, water cooled, 15.5 cm inner diameter stainless steel chamber with radiantly heated graphite sample holder. The radiation is coupled into the chamber with a TM_{01} rectangular to circular waveguide adapter through a silica window. The chamber operates at 1 to 5 kPa, with typical gas mixtures being 0.5% CH_4 in H_2. Growth temperatures ranged from 450 to 980°C (IR pyrometer), with variation of 50 to 75°C across the 10 cm silicon substrate.

The higher pressure system (20 to >100 kPa) uses the same 1.5 kW magnetron head coupled through a three stub tuner into a custom designed cylindrical high pressure TM_{010} 2.45gHz cavity. The microwave power is coupled directly into the gas flowing through a 12 mm quartz flow tube passing through the center of the cavity. This system couples 1.2 to 1.5 kW into the flowing gas and produces a plasma flame. The flame is forced out of the quartz tube by flows of 20 to 50 l/min of a 2/1 Ar/H_2 mixture with CH_4 held at the same ratio to H_2 as with the MPACVD chamber. The substrates in this system were typically 4x4x25mm rectangular polycrystalline Si_3N_4 bars held at right angles to the plasma front or 0.5 cm radius molybdenum hemispheres. All substrates were mounted on a water-cooled fixture and temperatures were monitored by an IR pyrometer.

Polycrystalline particles and films were examined by scanning electron microscopy and Raman scattering spectroscopy.



3. RESULTS AND DISCUSSION

Nucleation and microstructure effects in the low pressure (1.6 to 5.3 kPa) microwave plasma assisted diamond chamber have been described by a number of researchers. The most generally reported trends are the observation of (100) exposed faces on the diamond grains at higher hydrocarbon concentrations, switching to primarily (111) exposed crystalline planes at lower hydrocarbon concentrations for a fixed deposition temperature.[1,2] A significantly different microstructure occurs when the film growth becomes defect renucleation dominated and highly twinned (110) global orientation is obtained[3]. Such (110) oriented films have been obtained by a number of researchers under conditions with low hydrocarbon concentrations and added oxygen.[3,4] In this work these same trends in diamond film microstructure have been observed at all deposition pressures. The primary effects associated with increasing pressure have been a significant increase in the observed film growth rate for a given gas composition and substrate temperature and a dependence of the growth process upon gas flow dynamics.

At a substrate temperature of 950°C the growth rate of polycrystalline diamond was nominally 0.6 microns/hr at 4 KPa, 3-5 microns/hr at 25 kPa, and 10-20 microns/hr at 100 kPa pressure for reaction mixtures containing a methane to hydrogen ratio of about 0.5%. The increase in growth rate with pressure is associated with the arrival rate of the reactive species forming the diamond particles on the substrate surface, but has not been quantified due to the dependence of the growth process on the flow dynamics.

The effects of reactant composition and temperature on the microstructure of the diamond particles formed in the microwave systems were basically the same at all pressures and permits a phenomenological description of the effects of growth conditions to be postulated. Figure 1 (a-l) is a series of SEM micrographs showing the progression of microstructure types associated with the deposited carbon films as a function of distance from the locus of the plasma ball in the low pressure system, and the feather of the plasma flame in the high pressure system. At greater distances from the most intense plasma region there is a decrease in both the surface temperature of the growing particles and the concentration of the radical and atomic species associated with the growth process. In a steady-state system the progression would coincide with increasing temperature and an increasing hydrogen atom to hydrocarbon radical ratio.

At the greatest distance from the plasma (lowest temperature, lowest hydrogen atom, highest unreactive hydrocarbon content) very high nucleation density produced a continuous amorphous carbon film with hemispherical surface protrusions. Nearer to the plasma the nucleation density drops and the particles become distinct and microcrystalline. Raman spectra of the material in this regime show diamond and some sp2 bonded carbon. The particles have very high defect densities with the dominance of surface energy constraints being obvious from the spherical appearance of the particles.

Moving still nearer to the plasma, the particles remain generally spherical, but {100} faces appear and the Raman spectrum shows a decrease in graphitic carbon. The {100} facets become more pronounced as the concentration of hydrogen atoms and etching species increase in toward the center of the plasma. In this region surface energy is competing with the growth and etch rates of the sp2 and sp3 solid carbon to determine the microstructure. The particles still tend to a spherical shape, but preferential <111> direction growth is favoring the exposure of {100} faces.

In regions of greater plasma density, the surface temperature and hydrogen atom concentrations are higher and nucleation as well as defect generation become lower. The particles are more highly faceted, with cubo-octahedral shapes. In this regime the surface energy anisotropy between the crystalline planes is more significant and the particle microstructure becomes controlled by the relative reaction kinetics of growth and etching. The cubo-octahedral particles have the <110> direction being the long axis of fastest growth. This is consistent with the observation that the {110} plane of diamond has the lowest etching rate in hydrogen and oxygen.[5]

In the center of the plasma region the surface temperature and reactive etching species concentrations are the highest. In this regime, high etch rates discriminate against the less stable nucleation centers, favoring the formation of the characteristic five-fold twinned defect nuclei. This crystallographic defect is a successive multiple twinning on the {111} planes in a <211> direction around the <011> axis. Forming at a very fine scale, this defect continues to grow to produce the end member microstructure seen in Figure 1 which is dominated by the exposed {111} planes.

This phenomenological description is consistent with the observation that at growth temperatures near 650°C many films develop a characteristic global (110) orientation as renucleation on the initial film layer leads to increasing thickness[3]. Anisotropic etching and the apparent faster growth in the <110> direction favor global (110) orientation as does the availability of the low energy (111) slip plane twin defect which provides a low-energy site for preferential bonding of radical species, leading to an enhanced growth rate in the (110) orientation (Figure 2).

4. CONCLUSIONS

The growth rate of diamond films from microwave generated plasmas increases by over 40 fold between 4 and 100 kPa pressure with the same hydrocarbon/hydrogen gas ratio and substrate temperature. The film microstructure in the first fully developed continuous film layer is remarkably similar for films grown at low and high pressures and is consistent with a model based on surface energy effects and anisotropic growth. The model suggests that higher etching conditions favor growth along the <110> direction and that high nucleation-lower etching conditions favor growth in the <111> direction. Such films would have (111) and (100) planes exposed respectively.

5. ACKNOWLEDGEMENTS

Portions of this research were sponsored by the Office of Naval Research, Department of the Navy, Arlington, Virginia.

6. REFERENCES

1. K. Kobashi, K. Nishimura, Y. Kawate, and T. Horiuchi, Phys. Rev. B 38 4067 (1988).

2. K.V. Ravi, C.A. Koch, H.S. Hu, and A. Joshi, J. Mater. Res. vol 5, 2356 (1990).

3. J.F. DeNatale, A. B. Harker, and J.F. Flintoff, J. Appl. Phys 69(9), 6456-6460 (1991).

4. K. Kobashi, K. Nishimura, K. Miyata, K. Kumagai, and A. Nakue, J. Mater. Res. vol 5, 2469 (1990).

5. A. Zheng, H. Kanda, T. Ohsawa, and S. Yamaoka, J. Mat. Sci. Lett. 9, 331 (1990).

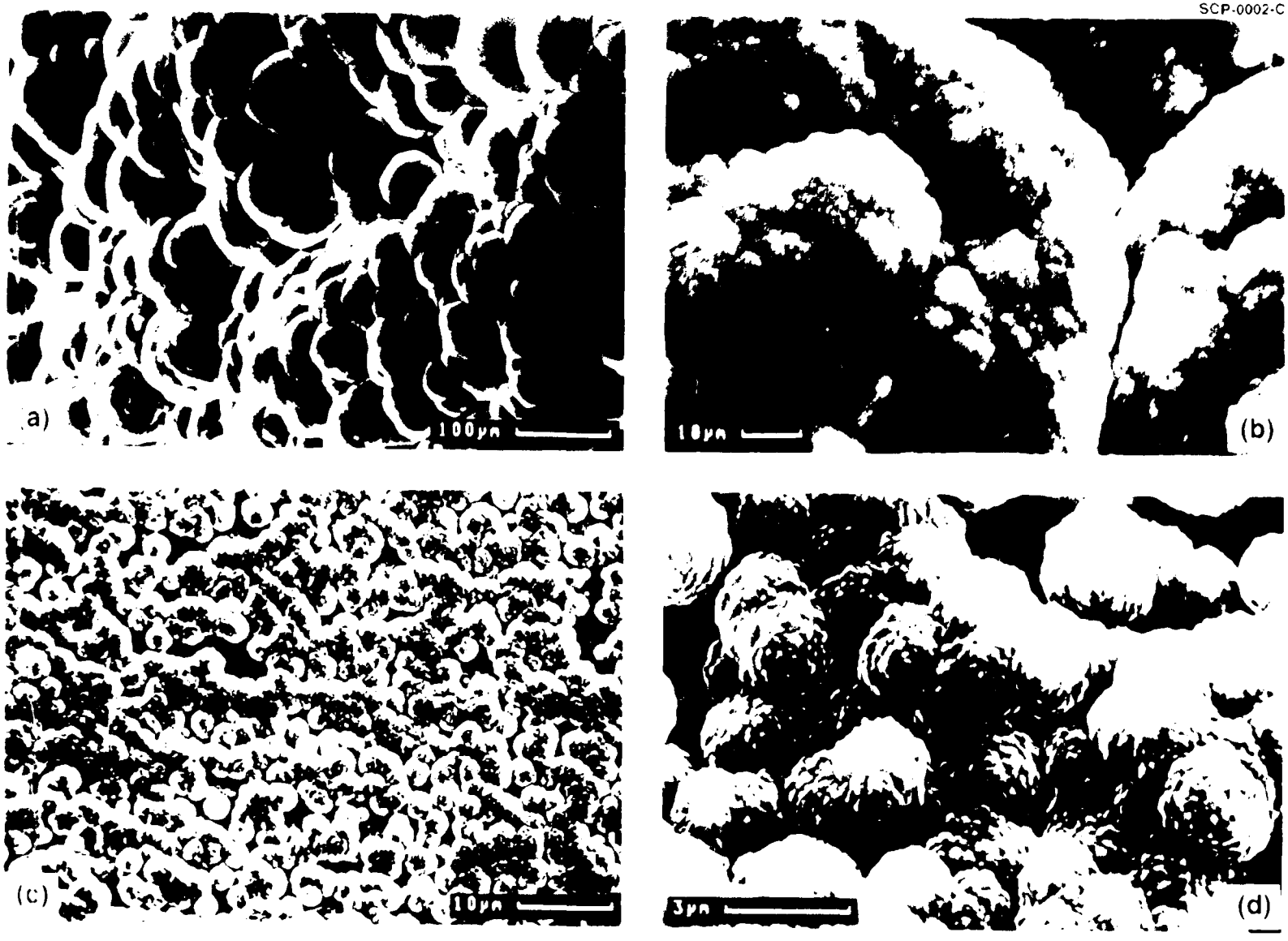


Figure 1 (a-d) SEM micrographs showing the change in polycrystalline diamond microstructure as a function of distance from the center of the growth plasma.

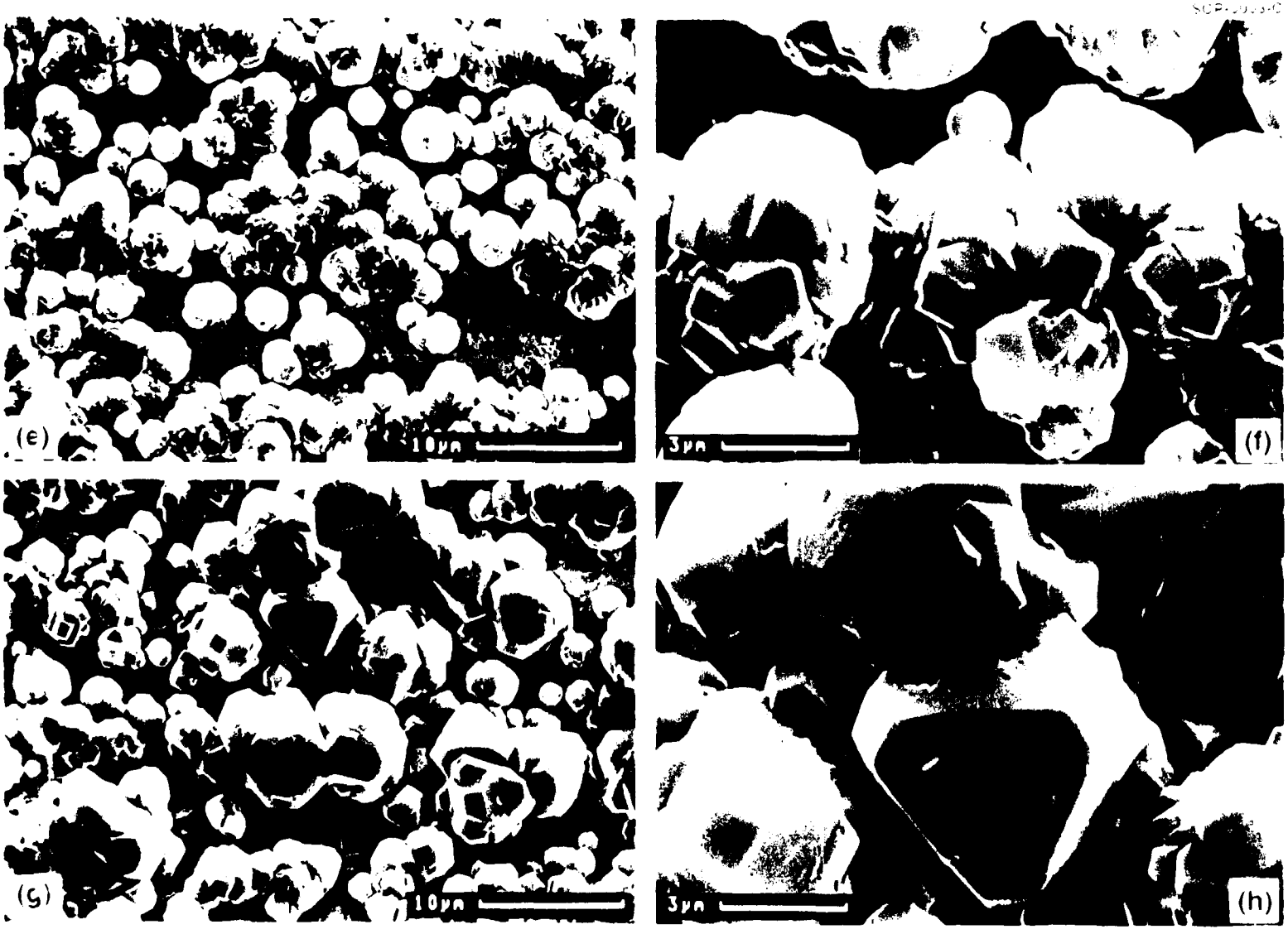


Figure 1 (e-h) SEM micrographs showing the change in polycrystalline diamond microstructure as a function of distance from the center of the growth plasma

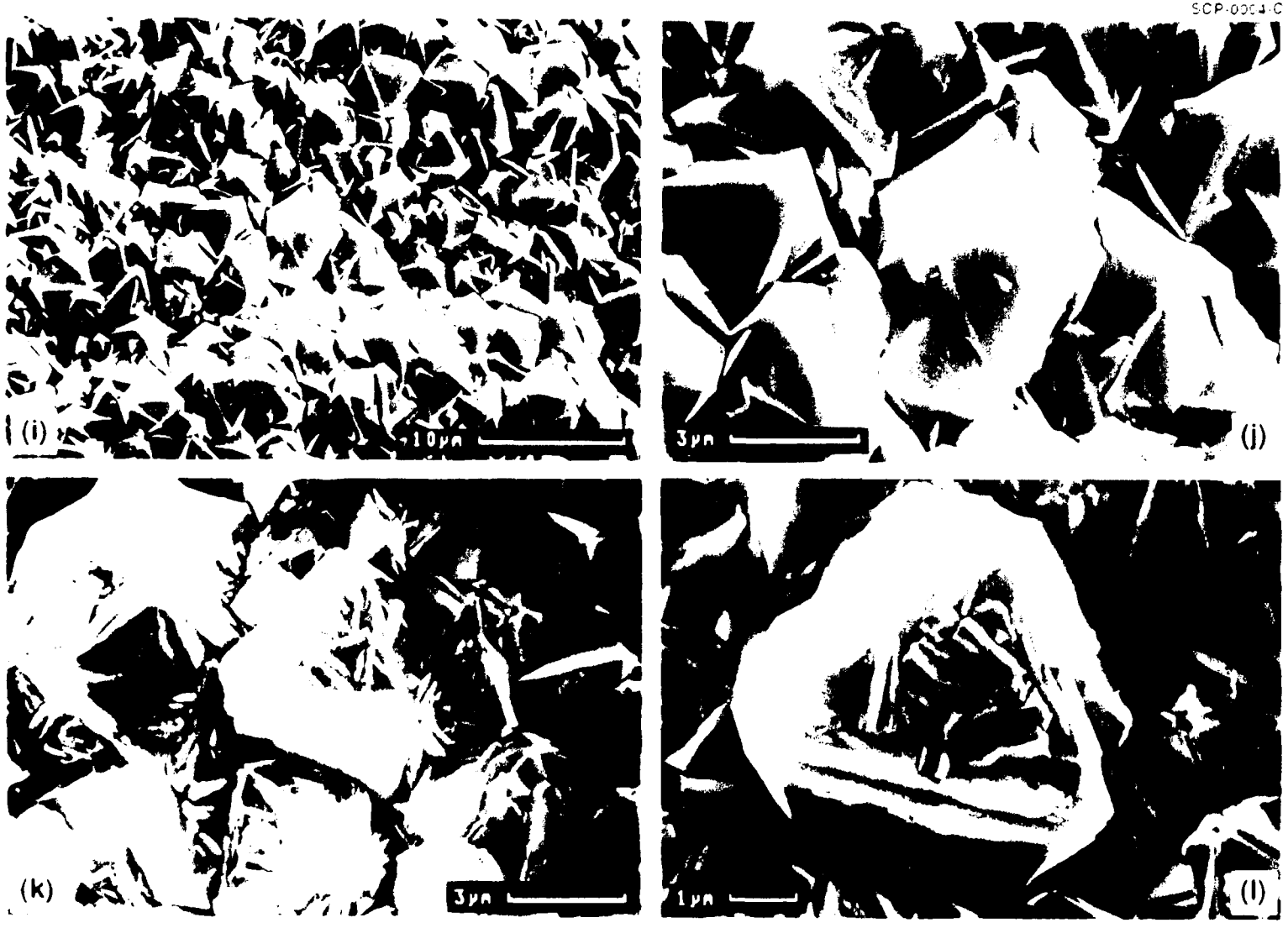


Figure 1 (i-l) SEM micrographs showing the change in polycrystalline diamond microstructure as a function of distance from the center of the growth plasma.

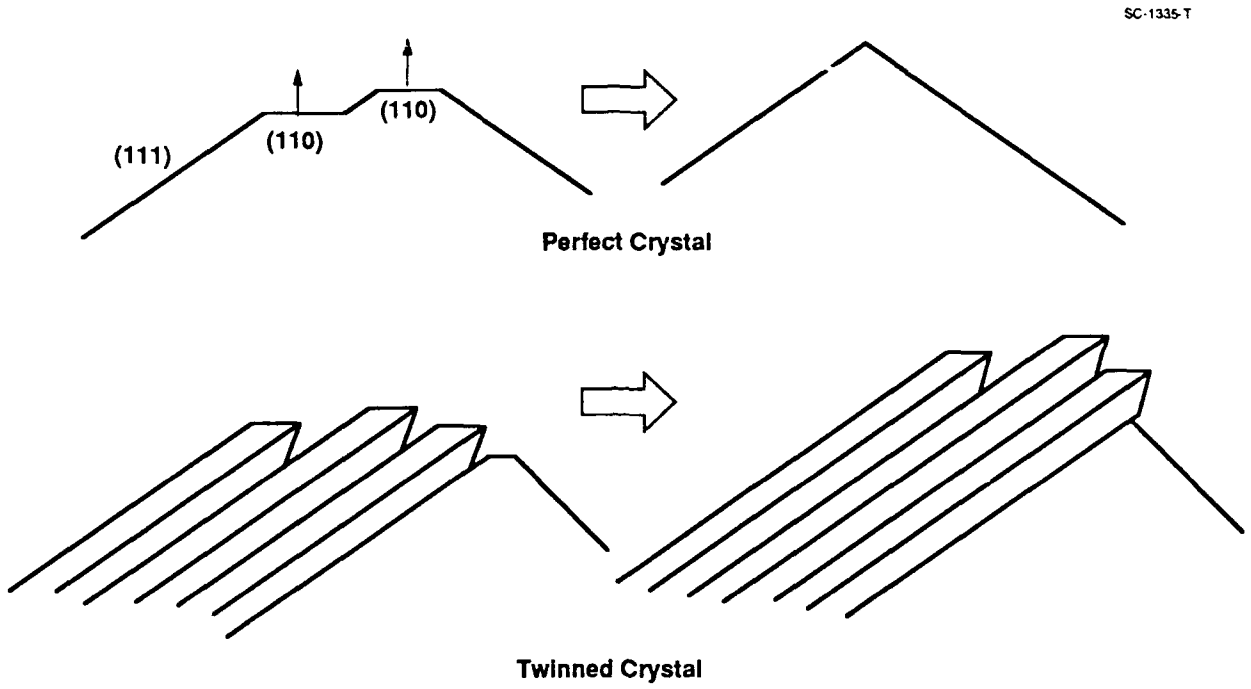


Figure 2. Schematic of a process favoring a (110) oriented growth surface propagation in multiply twinned diamond particles.